OKAYAMA University
Earth Science Reports,
Vol. 8, No. 1, 39-44, (2001)

Hydrogen and oxygen isotope ratios of thermal waters of Izu Peninsula, Shizuoka Prefecture, Japan

Daiju KOBYASHI and Masahiro YAMAMOTO

Department of Earth Sciences, Okayama University, 1-1 Tsushima-Naka 3, Okayama 700-8530, Japan

Hydrogen and oxygen isotope ratios of thermal waters from 42 hot springs in Izu Peninsula, Shizuoka Prefecture, range from -51.7 to -24.7‰ in δD and from -7.9 to -4.1‰ in $\delta^{18}O$, respectively. The isotope ratios suggest that most of the thermal waters in Izu Peninsula are essentially meteoric in origin. Significantly deviated from the normal meteoric waters are thermal waters from Yumigahama, Kumomi, and Shimogamo hot springs which may be mixtures of seawater and local meteoric waters, and thermal waters from Izusan and Imaihama whose oxygen isotope ratios may have become heavier by water-rock interaction.

Keywords: Hydrogen isotope ratio, Oxygen isotope ratio, Thermal water, Hot spring, Izu Peninsula, Shizuoka Prefecture

I. Introduction

The Japanese thermal water systems have been grouped into four major categories according to their isotope and major element chemistry: Arima type, Green Tuff type, coastal type and volcanic type thermal waters (Matsubaya *et al.*,1973; Sakai and Matsubaya, 1974; Sakai and Matsubaya, 1977). Matsubaya *et al.* (1973) determined hydrogen and oxygen isotope ratios of water and sulfur and oxygen isotope ratios of sulfate and major constituents of the thermal waters collected from hot springs located on the eastern coast of Izu Peninsula (Atami, Ito, Katase, *etc.*) and stated that although most of the thermal waters in Izu Peninsula were closely related to Green Tuff formations, those along the ocean coasts were considered to be mixtures of oceanic and local meteoric waters. For the thermal waters from Shimogamo near the southern coast of Izu Peninsula, Mizutani and Hamasuna (1972) concluded that they were mixtures of local meteoric waters and deep-seated hydrothermal brines of seawater origin.

In order to study the thermal water system of Izu Peninsula more extensively, we have collected thermal waters from forty-two hot springs in Izu Peninsula including those studied by previous workers and determined hydrogen and oxygen isotope ratios and major constituents of the waters. In the present paper, brief discussion on the isotope ratios is given. Detailed discussion on the major element chemistry will be given in the following paper.

II. Samples and analytical procedures

Location of the hot springs from which water samples were collected is shown in Fig. 1.

Major constituents were determined as follows: Na and K by flame photometry, Ca and Mg by ICP-AES, Cl and SO_4 by ion chromatography, and HCO_3 by pH4.8-acidimetry.

Hydrogen and oxygen isotope ratios of water were determined at the Institute for Study of the Earth's Interior, Okayama University. For D/H measurements, water was reduced to H_2 using uranium metal. For $^{18}O/^{16}O$ analyses, water was equilibrated with tank CO_2. The results are given in conventional δ values as permil deviations from the standard, SMOW.

III. Results and discussion

Hydrogen and oxygen isotope ratios of thermal waters from hot springs of Izu Peninsula, Shizuoka Prefecture, are listed in Appendix 1, together with their temperatures, pH and concentrations of the major constituents. The TDS (total dissolved solids) of thermal waters of Izu Peninsula are in a wide range from 183mg/l for Komanoyu (#3) to 15,200mg/l for Yumigahama (#42). Following the classification by Frape *et al.* (1984), three waters from Yumigahama, Kumomi (#40) and Izusan (#1) are saline (TDS > 10,000mg/l), twenty-one brackish (TDS =1,000-10,000mg/l), and eighteen fresh (TDS < 1,000mg/l).

Hydrogen and oxygen isotope ratios of the thermal waters range from -51.7 to -24.7‰ in δD and from -7.9 to -4.1‰ in $\delta^{18}O$, respectively. Here again Komanoyu is the lowest and Yumigahama is the highest both in δD and $\delta^{18}O$. All the isotope data are plotted on the δD - $\delta^{18}O$ diagram in

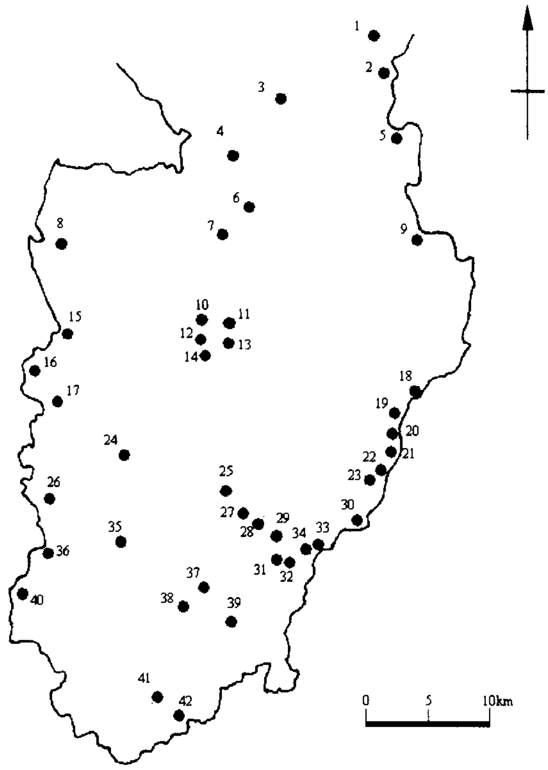

Fig. 1. Distribution of hot springs in Izu Peninsula. Numbering is approximately from north to south.
1: Izusan, 2: Atami, 3: Komanoyu, 4:Izunagaoka, 5:Ajiro, 6: Ohito, 7:Shuzenji, 8: Heda, 9: Ito, 10: Funabara, 11: Tsukigase, 12: Yoshina, 13: Sagasawa, 14: Yugashima, 15: Toi, 16: Yagisawa, 17: Ugusu, 18: Akazawa, 19: Okawa, 20: Hokkawa, 21: Atagawa, 22: Katase, 23: Shirata, 24: Neginohata, 25: Odaru, 26: Dogashima, 27: Konabe, 28: Yugano, 29: Mine, 30: Inatori, 31: Yatsu-1, 32: Yatsu-2, 33: Imaihama, 34: Kawazuhama, 35: Osawa, 36: Matsuzaki, 37: Shimoda (Aitama), 38: Kannon, 39: Kochi, 40: Kumomi, 41: Shimogamo, and 42: Yumigahama.

Fig. 2.

The isotope ratios of the local meteoric waters at Izu Peninsula were in the ranges from -49.5 to -40.3‰ in δD and from -8.0 to -6.8‰ in $\delta^{18}O$ (Matsubaya *et al.*, 1973; Mizota and Kusakabe, 1994). At Shimogamo in the southernmost Izu Peninsula, a little higher $\delta^{18}O$ value of -6.2‰ was observed for a river water (Mizutani and Hamasuna, 1972). Therefore, it is shown in Fig. 2 that most thermal waters are in the meteoric water range of Izu Peninsula, although plotted somewhat below the Japanese meteoric water line. Significantly deviated from the meteoric water line are thermal waters from Yumigahama, Kumomi, Shimogamo, Imaihama (#33) and Izusan. Of these, Yumigahama, Kumomi and Shimogamo are on the mixing line of the local meteoric water and seawater. Imaihama and Izusan are not on the line, but plotted below the mixing line. Komanoyu, which has the lowest δD and $\delta^{18}O$ values, is also below the mixing line.

Next, to more clearly demonstrate the participation of seawater in forming thermal waters, the $\delta^{18}O$ values of thermal waters are plotted against the Cl concentrations in Fig. 3. The mixing line is drawn between seawater ($\delta^{18}O$ = 0‰, Cl = 19,000mg/l) and the assumed average meteoric water of Izu Peninsula ($\delta^{18}O$ = -7.5‰, Cl = 0mg/l). Yumigahama, Kumomi and Shimogamo are plotted close to the mixing line. Together with the δD-$\delta^{18}O$ relationship shown in Fig. 2, this strongly suggests that they are mixtures of seawater and the local meteoric waters. It must be mentioned, however, that they are not simple mixtures of the present seawater and meteoric water, because, as seen from Appendix 1, the Ca/Na ratios of the thermal waters are significantly higher than the ratio of the present seawater. The thermal water of Izusan is not on the line, but somewhat below the mixing line. Matsubaya *et al.* (1973) also found that the thermal waters from Atami and Ito lay below the mixing line between seawater and the local meteoric waters, although the present results on the thermal waters from the same hot springs indicate the normal meteoric isotope ratios. They concluded that those thermal waters may be mixtures of seawater-derived brines of normal isotopic values and meteoric thermal waters of relatively high salt concentration. The thermal water of Izusan in the

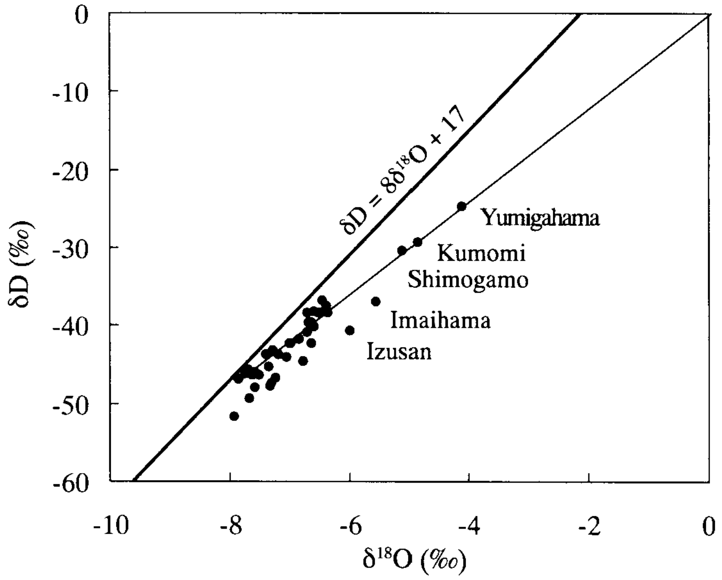

Fig. 2. Relationship between hydrogen and oxygen isotope ratios of thermal waters from hot springs in Izu Peninsula, Shizuoka Prefecture. Thick line: Japanese meteoric water line. Thin line: mixing line between seawater and meteoric waters at Izu Peninsula.

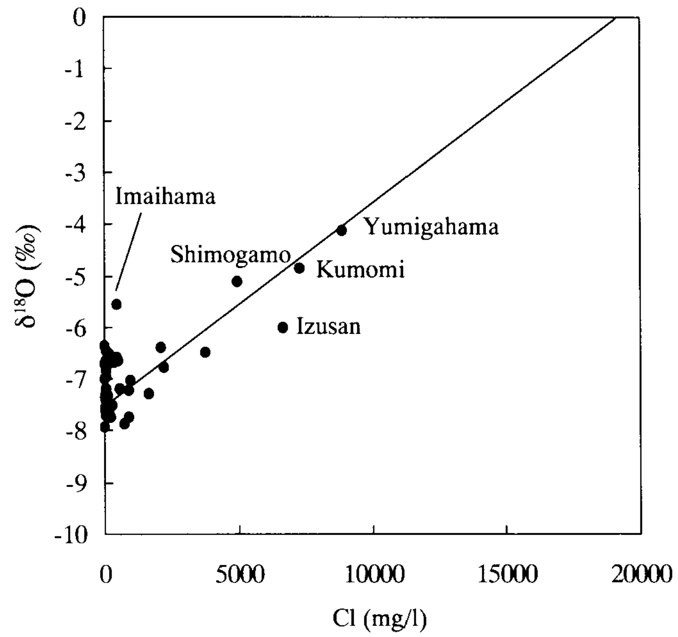

Fig. 3. Relationship between oxygen isotope ratio and Cl concentration of thermal waters from hot springs in Izu Peninsula, Shizuoka Prefecture. Mixing line is between seawater and average meteoric water of Izu Peninsula.

present study may be interpreted in the same way.

Imaihama, on the contrary, is plotted above the mixing line in Fig. 3. The Cl concentration of Imaihama was very low, 437mg/l. Therefore, the heavy $\delta^{18}O$ of -5.6‰ of the thermal water may be due to water-rock interaction rather than mixing of seawater. Although Imaihama is grouped in the fresh thermal waters (TDS = 976mg/l), the ratios of Na, K, Ca, and SO_4 to Cl are similar to those of seawater, which suggests the dissolved constituents are mainly from seawater. Most fresh thermal waters plotted close to Y-axis are above the mixing line. This may be the result of oxygen isotope shift during water-rock interaction as Imaihama.

The thermal waters with the Cl concentration more than 2,000mg/l (Atami, Ajiro and Inatori) lie near the mixing line, suggesting the contribution of seawater to their isotope ratios.

Acknowledgments: Mass spectrometry of hydrogen and oxygen isotope ratios was done at the Institute for Study of the Earth's Interior, Okayama University, under the auspices of Prof. M. Kusakabe. The authors thank many people for their kind help in collecting water samples.

References

Frape, S. K., Fritz, P. and McNutt, R. H. (1984) Water-rock interaction and chemistry of groundwater from the Canadian Shield. *Geochim. Cosmochim. Acta*, **48**, 1617-1627.

Mason, B. and Moore, C. B. (1982) *Principles of Geochemistry, 4th Ed.* John & Wiley Sons, 344pp.

Matsubaya, O., Sakai, H., Kusachi, I. and Satake, H. (1973) Hydrogen and oxygen isotopic ratios and major element chemistry of Japanese thermal water systems. *Geochem. J.*, **7**, 123-151.

Mizota, C. and Kusakabe, M. (1994) Spatial distribution of δD-$\delta^{18}O$ values of surface and shallow groundwaters from Japan, south Korea and east China. *Geochem. J.*, **28**, 387-410.

Mizutani, Y. and Hamasuna, T. (1972) Origin of the Shimogamo geothermal brine, Izu. *Bull. Volcanol. Soc. Jpn. 2nd Ser.,* **1**, 123-134 (in Japanese).

Sakai, H. and Matsubaya, O. (1974) Isotopic geochemistry of the thermal waters of Japan and its bearing on the Kuroko ore solutions. *Econ. Geol.*, **69**, 974-991.

Sakai, H. and Matsubaya, O. (1977) Stable isotopic studies of Japanese geothermal systems. *Geothermics*, **5**, 97-124.

Appendix 1. Chemical compositions and isotope ratios of thermal waters in Izu Peninsula, Shizuoka Prefecture, Japan

No.*	Hot spring	Date	t	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	TDS	δD	$\delta^{18}O$
			°C		mg/l								‰	
1	Izusan	1999/8/4	68.1	7.28	1500	65.0	2940	39.2	6650	804	25.2	12100	-40.7	-6.0
2	Atami	1999/8/4	40.6	7.32	977	107	595	1.7	2230	149	32.9	4200	-44.5	-6.8
3	Komanoyu	1999/8/5	38.9	9.05	40	0.8	6.6	n.d.	12.4	40.4	52.6	183	-51.7	-7.9
4	Izunagaoka	2001/5/16	54.4	8.72	190	2.4	10.7	n.d.	114	190	50.6	615	-49.3	-7.7
5	Ajiro	2001/5/16	44.4	7.40	1640	25.6	1060	10.0	3780	386	28.8	6960	-38.4	-6.5
6	Ohito	1999/8/6	50.7	7.66	109	10.0	35.3	1.1	84.4	131	85.7	500	-47.4	-7.3
7	Shuzenji	1999/8/5	54.3	8.57	126	2.9	15.5	0.2	101	100	65.2	463	-47.8	-7.3
8	Heda	2001/5/18	48.8	8.61	641	8.4	150	n.d.	189	1410	31.3	2470	-46.3	-7.6
9	Ito	1999/8/4	49.4	8.17	210	6.5	120	1.6	250	297	21.9	952	-46.1	-7.7
10	Funabara	1999/8/5	46.9	7.89	209	3.5	43.4	0.3	98.5	308	39.1	732	-46.0	-7.6
11	Tsukigase	1999/8/6	43.5	8.43	75	3.2	89.1	0.6	21.6	260	39.4	524	-47.9	-7.6
12	Yoshina	2001/5/17	46.3	8.47	175	6.0	29.8	0.1	44.5	327	40.4	663	-45.6	-7.7
13	Sagasawa	2001/5/17	52.9	8.08	214	8.5	29.0	n.d.	45.3	450	44.5	833	-45.7	-7.7
14	Yugashima	1999/8/5	47.1	8.28	248	9.5	230	0.2	56.1	854	14.4	1450	-45.9	-7.7
15	Toi	2001/5/16	48.0	7.78	203	6.6	336	0.9	291	901	19.1	1800	-46.3	-7.5
16	Yagisawa	1999/8/5	28.9	7.55	363	7.6	389	3.2	591	780	23.6	2190	-43.6	-7.2
17	Ugusu	1999/8/5	50.9	9.14	69	3.3	663	0.3	15.8	1660	14.5	2450	-45.2	-7.4
18	Akazawa	2001/5/16	51.3	7.27	291	7.0	546	0.6	741	699	14.3	2330	-46.9	-7.9
19	Okawa	2001/5/16	54.0	7.87	815	12.6	164	0.7	935	627	64.4	2670	-45.7	-7.7
20	Hokkawa	1999/8/4	84.6	7.30	962	43.5	431	17.0	1630	454	140	3790	-43.2	-7.3
21	Atagawa	1999/8/4	91.9	8.27	835	70.0	95.1	2.0	936	475	111	2720	-46.6	-7.2
22	Katase	2001/5/16	47.1	7.72	190	16.2	67.4	13.6	338	133	124	939	-39.6	-6.7
23	Shirata	2001/5/16	51.2	7.90	768	45.0	163	2.7	974	518	172	2720	-44.1	-7.0

(continued)

No.*	Hot spring	Date	t	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	TDS	δD	$\delta^{18}O$
			℃					mg/l					‰	
24	Neginohata	2001/5/18	38.9	7.45	125	4.0	329	n.d.	36.5	1090	10.5	1620	-43.6	-7.4
25	Odaru	1999/8/4	41.6	8.22	65	2.8	93.0	0.5	26.0	257	23.5	506	-42.3	-7.0
26	Dogashima	1999/8/5	36.2	9.37	100	4.1	11.7	0.4	40.1	97.9	123	513	-42.2	-6.6
27	Konabe	2001/5/17	39.8	8.03	195	8.2	203	0.1	44.4	758	14.6	1270	-42.2	-7.0
28	Yugano	2001/5/17	56.2	7.74	195	6.6	195	0.1	46.8	747	21.2	1260	-41.7	-6.9
29	Mine	1999/8/6	61.8	7.79	338	32.2	61.0	1.8	532	83.6	48.4	1190	-39.6	-6.6
30	Inatori	1999/8/4	62.2	7.92	1210	80.0	470	17.8	2120	567	55.4	4590	-37.4	-6.4
31	Yatsu-First	2001/5/17	94.3	7.96	380	36.6	37.7	0.3	436	186	54.1	1260	-38.2	-6.6
32	Yatsu-Second	2001/5/17	51.9	7.98	153	13.8	31.2	0.4	187	102	73.1	624	-38.3	-6.5
33	Imaihama	2001/5/16	43.0	7.68	282	30.9	39.7	1.4	437	74.2	37.8	976	-36.9	-5.6
34	Kawazuhama	2001/5/16	48.0	6.94	340	31.2	35.3	1.2	430	124	65.0	1110	-40.2	-6.6
35	Osawa	1999/8/6	43.8	8.32	267	7.0	54.5	1.1	29.5	523	73.8	985	-40.9	-6.7
36	Matsuzaki	1999/8/5	54.4	8.60	322	11.2	314	2.0	81.5	1260	19.2	2060	-43.7	-7.2
37	Shimoda(Aitama)	1999/8/6	43.5	9.20	47	1.5	7.3	0.5	16.2	33.2	83.1	222	-38.3	-6.4
38	Kannon	2001/5/17	50.0	9.22	59	1.5	1.6	0.1	9.9	29.1	113	321	-38.4	-6.7
39	Kochi	2001/5/17	48.1	8.18	62	2.1	10.9	0.1	34.6	92.5	65.5	304	-36.8	-6.5
40	Kumomi	1999/8/6	42.1	7.17	2020	40.1	2460	69.8	7290	664	20.5	12600	-29.3	-4.9
41	Shimogamo	1999/8/4	68.0	7.35	2190	196	1100	6.5	4980	79.7	35.5	8690	-30.3	-5.1
42	Yumigahama	2001/5/16	68.9	7.60	4070	363	1550	5.6	8910	137	18.8	15200	-24.7	-4.1
	Seawater**			8.00	10600	380	400	1270	19000	2650	140	34400	0.0	0.0

*Location No. shown in Fig. 1.

**Mason and Moore (1982)